

METAL-ORGANIC ARCHITECTURES FOR ENERGY STORAGE AND CONVERSION

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INTRODUCTION

Metal-organic architectures are emerging as particularly attractive host-guest materials for chemical energy storage and conversion. Chemical functionality, cavity size, and shape can be readily tuned by manipulating the organic moieties within these hybrid materials. With this ability to impart a high level of control over the final construct, these materials have the potential to revolutionize fields such as solar energy harvesting and conversion, size- and enantioselective catalysis, and fuels storage.

RESULTS

Solution phase assemblies have particularly strong promise in light harvesting applications as well as oxidative catalysis. The complete solution phase structural characterization of two porphyrin-based supramolecular systems will be presented: a series of porphyrin prisms¹ and a series of catalytic porphyrin box structures.² SAXS analysis gives us the overall size (radius of gyration, R_g) of the discrete assembly which we can distinguish from its components as well as higher oligomeric species. Additionally, scattering at higher q -values (WAXS) and the subsequent PDF analysis resolves metal-metal distances that are characteristic markers for identifying the structure of the assembly (Figure 1).

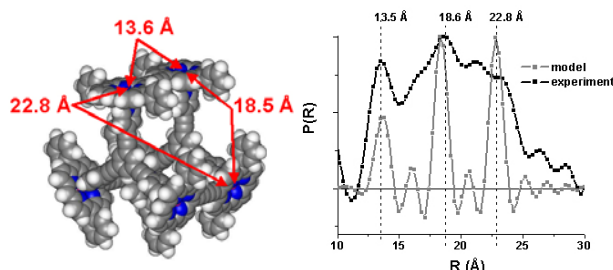


Figure 1. Model of prism assembly labeled with relevant metal-metal distances (left). Modeled and experimental PDF plot of wide-angle solution scattering (right).

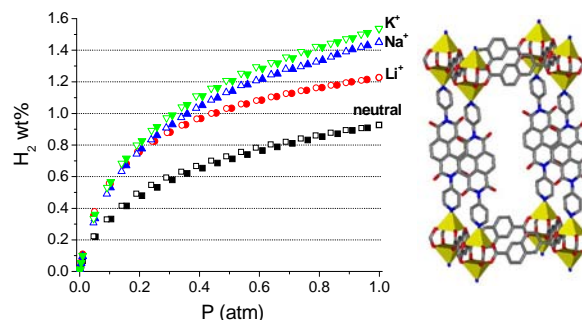


Figure 2. Low-pressure H₂ adsorption (left) of neutral and alkali-metal cation doped MOF structure (right).

To specifically address hydrogen storage concerns, we have developed a new class of mixed-ligand metal-organic frameworks (MOFs) of the general formula $\text{Zn}_2(\text{dicarboxylate})_2(\text{dipyridyl})$.³ Several of these materials can be chemically reduced in the solid state by common reductants such as lithium naphthalenide or through direct contact with lithium metal. One structure in particular exhibits striking hysteresis in the N₂ adsorption isotherm, suggesting dynamic framework behavior of the reduced material that is not observed in the neutral MOF.⁴ The reduced framework exhibits significantly enhanced H₂ uptake and isosteric heat of adsorption. Notably, the striking increase in H₂ uptake cannot be solely attributed to H₂-Li⁺ interactions, and is most likely augmented by increased ligand polarizability and framework displacement effects. Recently, this method has been generalized to new framework materials as well as other alkali metal cations (Figure 2).⁵

REFERENCES

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